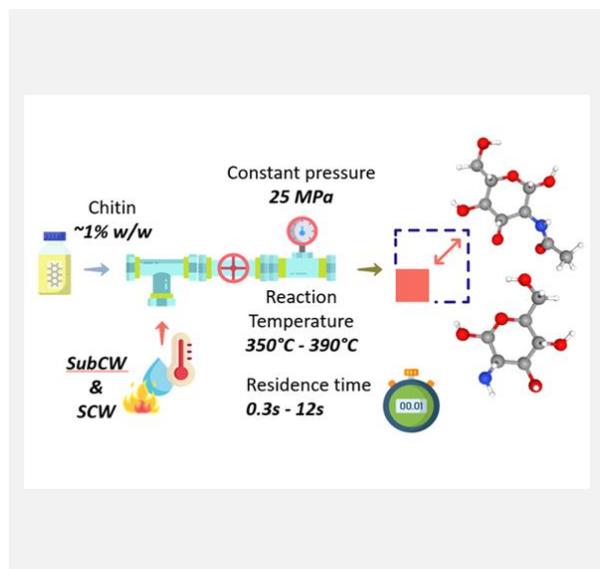


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Chitin ((1,4)- β -N-acetylglucosamine) is the second most widespread bio-polymer worldwide. Its high crystallinity and low solubility limit the exploitation of its antimicrobial, non-toxic and biodegradable properties, among others. So far, batch reactors and residence times longer than 1min with sub- and supercritical water have been tested to depolymerize chitin. In this work, we investigate the influence of temperature and residence time on chitin transformation in sub- and supercritical water (25MPa, 350 °C to 385 °C), using ultrafast continuous reactors (0.3s to 12s). Within the range studied, chitin gasification above 30% was detected when operating at high temperature ($T \geq 376$ °C) and a long residence time ($t \geq 5$ s). At these conditions, mean particle size of water-insoluble fraction was also reduced to ca. 280 nm. By-products such as glycolaldehyde, acetic acid and 5-HMF were identified in the water-soluble fraction, indicating the presence of side reactions.

Introduction

After cellulose, chitin is the second most widespread biopolymer worldwide. Its best-known applications, thanks to its antibacterial, toxicological and biocompatibility properties, are oriented to the medical and pharmaceutical industry, cosmetics, agriculture, and water treatment, among others. Being a biopolymer, chitin is formed by [β -1,4-poly(n-acetyl-D-glucosamine)] units, which can be treated to obtain oligomers and monomers, N-acetylglucosamine (depolymerization) and glucosamine (deacetylation). These monomers constitute nitrogen containing building blocks that open the way to sea-waste biorefinery for obtaining molecules of interest, such as furan-based monomers or amines [1].

The physicochemical properties (density, viscosity, diffusivity, ionic product, and dielectric constant) of water vary drastically around the critical point (374 °C and 22 MPa); which gives it versatility to be used as a reaction and reagent medium altering its autoionization. In supercritical conditions (SCW) the concentration of $[H^+]$ and $[OH^-]$ ions is low ($\sim 10^{-9}$) favoring radical reactions, while the subcritical medium (SubCW) favors ionic reactions generating high ion concentrations ($\sim 10^{-5}$) [2]. Studies have shown that chitin, like cellulose, can be dissolved and hydrolyzed in sub- and supercritical water thanks to the change on its properties; however, due to its high crystallinity, this process occurs less easily [3]. Processes in the literature have used SubCW and SCW technology in batch-type systems as pre-treatments, managing to dissolve crab chitin in times of up to 1 minute [3]. However, degradation compounds (char) have been obtained or even the prevalence of side-reactions (5-HMF formation) competing with hydrolysis has been observed (depending on the reaction conditions) [4].

Objective

The present work aims to investigate the mechanisms of chitin transformation in SubCW and SCW media, using ultrafast continuous reactors. Special attention is paid to the effect of

residence time and reaction temperature on the solubilization and depolymerization processes.

Methodology

Experimental set-up

Commercial α -chitin from shrimp shells (coarse flake, Sigma Aldrich, 99% purity) was ground in a ball mill to a mean particle size ($d_{50,v}$) of 75 μ m. During the milling process, β -chitin is formed. The ground β -chitin was subjected to hydrolysis conditions under SubCW and SCW and short reactor residence times (0.3-12s). The reaction processes were carried out in the continuously operated pilot plant (Figure 1) used by Cantero et al. (2015) for cellulose hydrolysis [5]. An aqueous suspension of the ground chitin was introduced into the system at room temperature and mixed with hot pressurized water stream to reach the selected reaction temperature and a chitin concentration in the reactor of ca. 1% w/w and 2%w/w. The reaction processes were carried out in a sudden expansion microreactor (SEMR) at constant pressure (25 MPa) and a temperature range between 350 °C and 390 °C, to achieve reaction times between 0.3s and 12s. The reaction mixture is then abruptly expanded in a decompression valve and cooled to room temperature to stop the reaction.

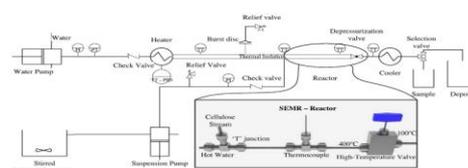


Figure 1. Experimental set-up (Cantero et al. 2015) [5].

Analytical methods

Raw material. Commercial chitin was characterized by elemental analysis, FT-IR, X-Ray diffraction and molecular weight by intrinsic viscosity analysis [6] to sketch a picture of the starting structure for the reaction process.

Reaction products. For characterization, the product was separated into water soluble and water insoluble fractions by centrifugation. The water-soluble fraction was characterized by HPLC chromatography, Total Organic Carbon (TOC), Total Nitrogen (TN) and pH. The water-insoluble fraction was characterized by elemental analysis (C, N, H), molecular weight [6], X-ray diffraction and particle size distribution by laser diffraction. Overall mass balance allowed to determine the chitin gasification fraction at the different operating conditions.

Results

The effect of reaction temperature and residence time on chitin depolymerization, and solid dissolution, is shown in Figure 2. When studying the influence of the residence time at constant temperature, an increase in the water-soluble fraction of the products was observed (19% in SCW conditions, and 8% in SubCW conditions). It was noticed that the SCW condition was more severe, observing a greater variation not only in the water-soluble fraction, but also a significant change in the gaseous fraction. The increase observed in the gas fraction is due mainly to the increase in reaction temperature rather than residence time in agreement with the behavior reported in the literature [4].

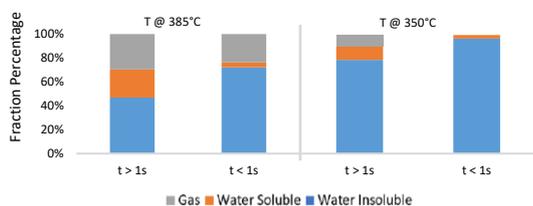


Figure 2. Influence of residence time and temperature on chitin processing.

The severity factor introduced by Overend and Chornet [7] for lignocellulosic biomass fractionation (Equation 1) has been used to consider the combined effect of temperature and time. The results in terms of severity factor are shown in Figure 3.

$$\text{Log}R_0 = \text{Log} \left(t \cdot \exp \left[\frac{T-100}{14.75} \right] \right) \quad (1)$$

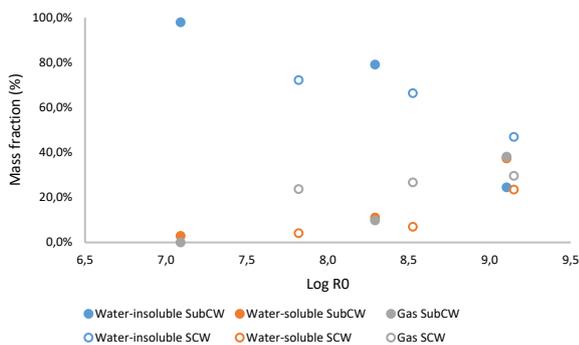


Figure 3. Water insoluble fraction, water soluble fraction, and gasification in terms of Severity Factor $\text{Log}R_0$.

Acknowledgements

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The water-insoluble fraction decreases at the exit of the reactor when severity factor is increased, whereas the trend of the water-soluble and gas fractions is the opposite. Although similar trends are observed for the subcritical region and the supercritical region, different correlations are identified in each region. This behavior can be due to the drastic change of the water pK_w in the range 350 °C - 385°C, and this fact must be considered in the severity factor calculation. In addition, when increasing severity factor above 9, the mean particle size as $d_{50,v}$ of the water insoluble fraction was reduced from ca. 75µm to approximately 0.28µm. Besides the analyzed size reduction, a change of structure was detected by FT-IR techniques, identifying, among others, a possible transition from a β -structure to an α -structure. Results obtained by elemental analysis showed a deviation from the characteristic C/N ratio of chitin (6.85) [8] of almost +2 points. These results and a change in coloration in the water insoluble fraction (from light yellow chitin fed to dark brown products) could indicate the presence of degradation compounds (e.g., humic compounds) and reaffirm the presence of side reactions, as reported in the literature [4].

Regarding the water-soluble fraction, it was observed that the composition profile was independent of the operating conditions, detecting the presence of glycolaldehyde, acetic acid, 5-HMF, and dihydroxyacetone (Figure. 4) in all the evaluated conditions. Their concentration, in agreement with results in Figure 2, increased with increasing operating temperature and residence time.

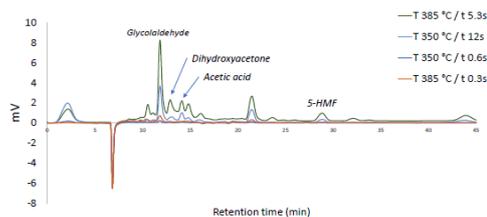


Figure 4. Liquid product composition profile.

Conclusions and on-going work

The results show that, within the studied range, chitin could not be fully depolymerized in sub and supercritical water and a solid product was get in all experimental conditions. Higher severity factors promoted gasification, particle size reduction of solid fraction and presence of by products as hint of side reactions competing with depolymerization. Also, the formation of humic acid is suggested due to the change in the visual appearance of the solid product (water-insoluble fraction).

Experimental work is being oriented to develop a specific correlation of the severity factor in the range 350°C-400°C. Moreover, characterization of solid, liquid and gas products will be studied deeply. For instance, a flash and a gas capture system has been implemented to characterize the gas phase by GC-MS.